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Theoretical studies of ionic liquids + nanoclusters as hybrid fuels

17 August 2016

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Aerospace Systems Directorate

Air Force Research Laboratory

This presentation contains information up to:

Outline

1. **Introduction**

2. **Boron nanoparticles/ionic liquid systems**
   a) theoretical model
   b) conventional solvents vs. ionic liquids
   c) improved dispersion via B-H functionalized surface

3. **Aluminum nanoparticles**
   a) production via ball milling
   b) surface chemistry of milling agents

4. **Summary and Conclusions**

5. **Acknowledgements**

Aerospace Systems Directorate

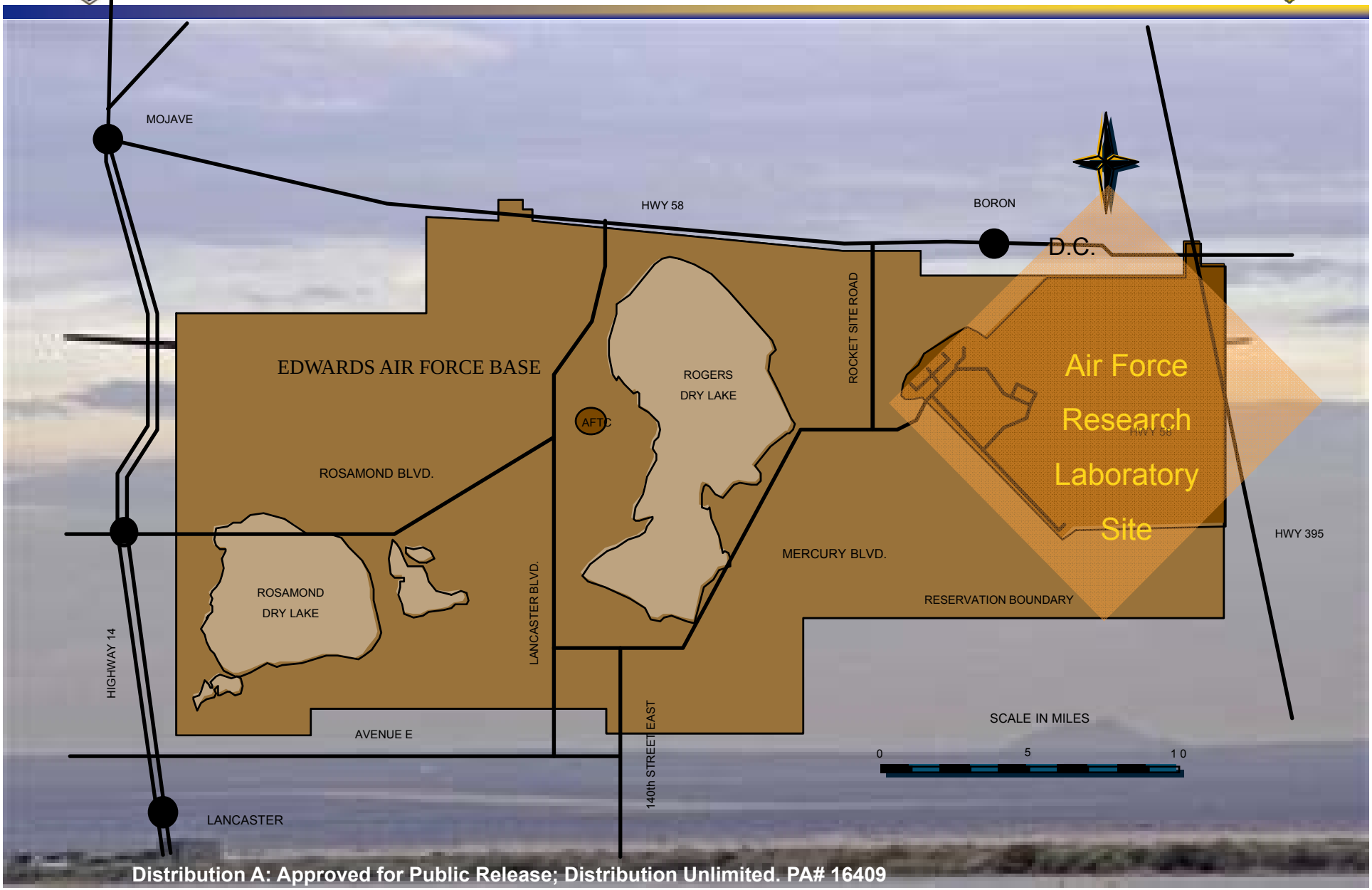
RQ-West (EAFB, CA)

- Rocket Engines & Motors
- Satellite Propulsion
- Combustion Devices
- Fuels and Propellants
- System Analysis
- R&D Rocket Testing

RQ-East (WPAFB, OH)

- Air Vehicle Structures
- Controls
- Turbine Engines
- Ramjet Engines
- Hypersonic Engines
- Aircraft Power
- Thermal Management
- Fuels and Propellants
- System Analysis

Edwards AFB



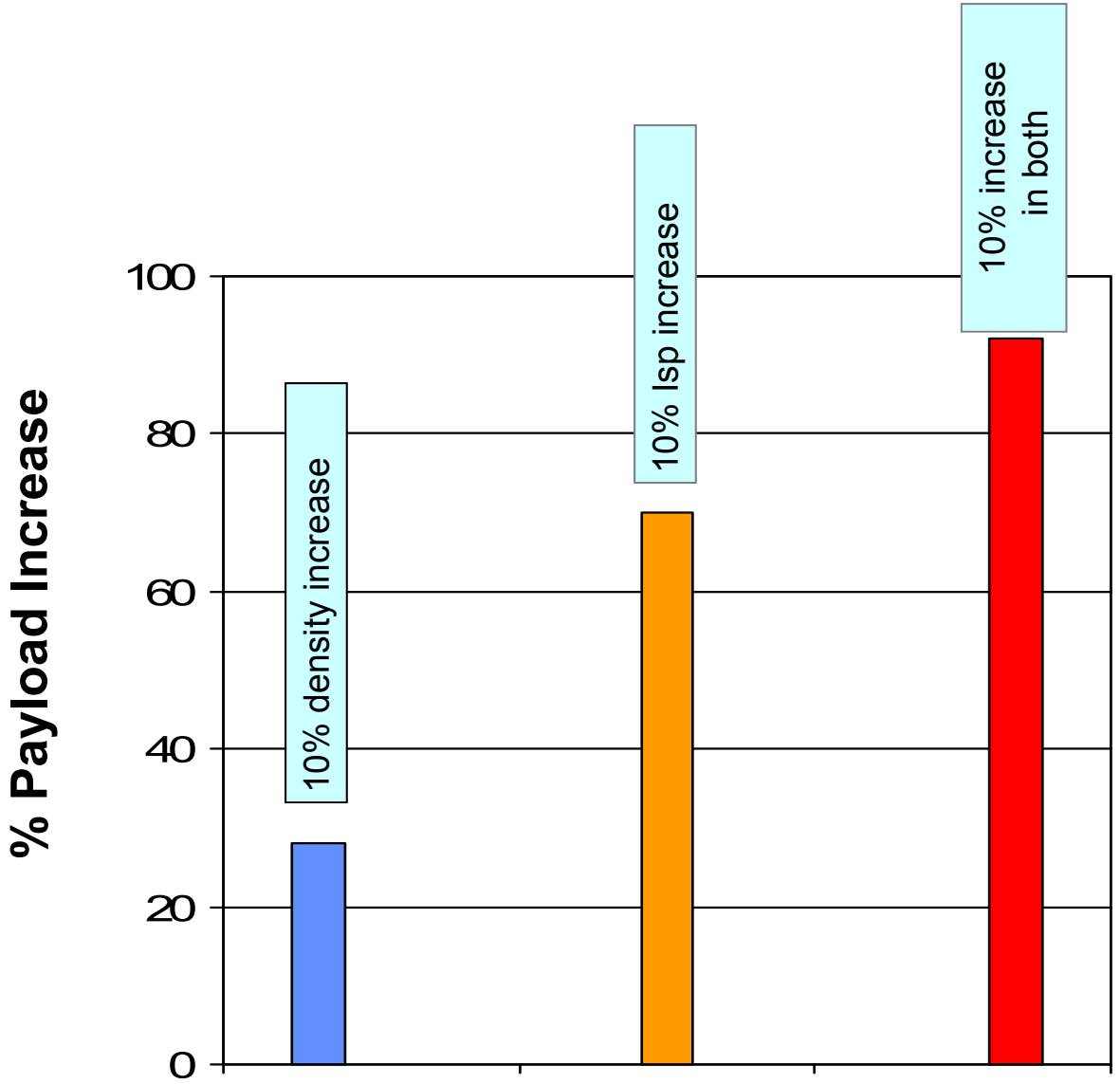
What We Are Doing

Identify and develop advanced chemical propellants for rocket propulsion applications

- **Isp (specific impulse) is a major metric of propellant performance**
- **Density can also be a significant contributor**




Why We Are Doing It



AF-M315 Monopropellant Class

AF-M315 monopropellants produced from ionic liquids

-Time consuming

- Expensive

Characteristic	Hydrazine	"IL-1"	"IL-2"
Melting Point (°C)	< 1.0	-50 (glass)	≈15
Vapor Pressure (torr)	14.3	< 0.1	< 0.1
Density (g/ml)	1.00	1.42	1.68
Toxicology			
Ames (mutagenic)	5/5 positive	2/5 positive	0/5 positive
LD50, rat (mg/kg)	60	367	325
Skin Irritation	Corrosive	Slight	Moderate

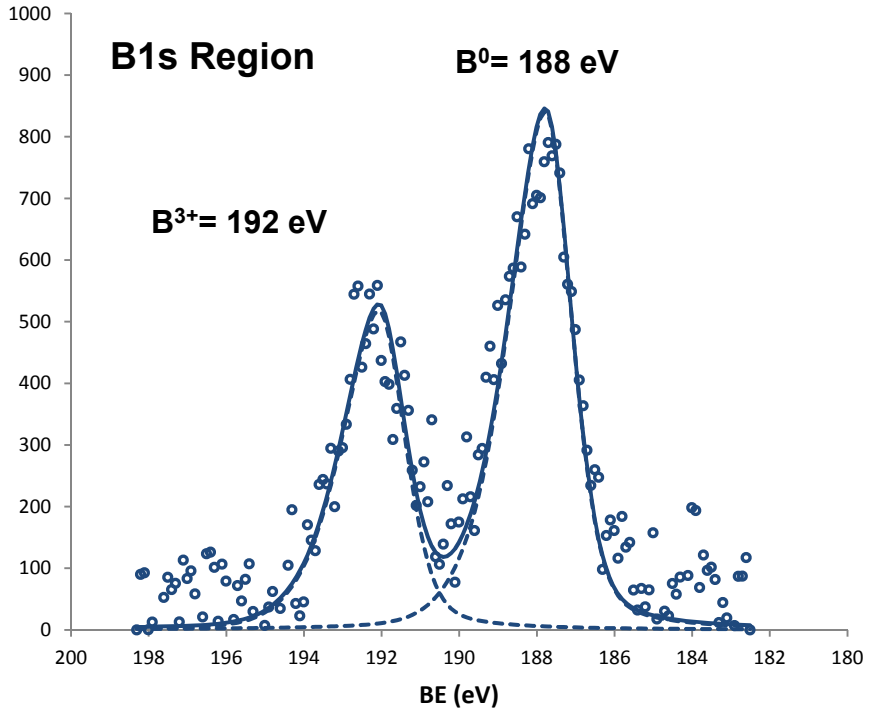
- Low hazard
- Low cost

IL/metal hybrid fuels

- **Bulk aluminum powder is a commonly used ingredient in solid propellants.**
  - large heat of combustion, enhanced burn rate, ...
- **Can Group 3A metals (B, Al) be utilized in liquid fuels?**
  - Particles must be small enough (nanoscale) to form stable colloidal suspensions
  - Resistant to formation of inert oxide surface layer to preserve energy density and ignition efficiency

IL/metal hybrid fuels

Boron nanoparticles (BNPs) phase separate from some solvents



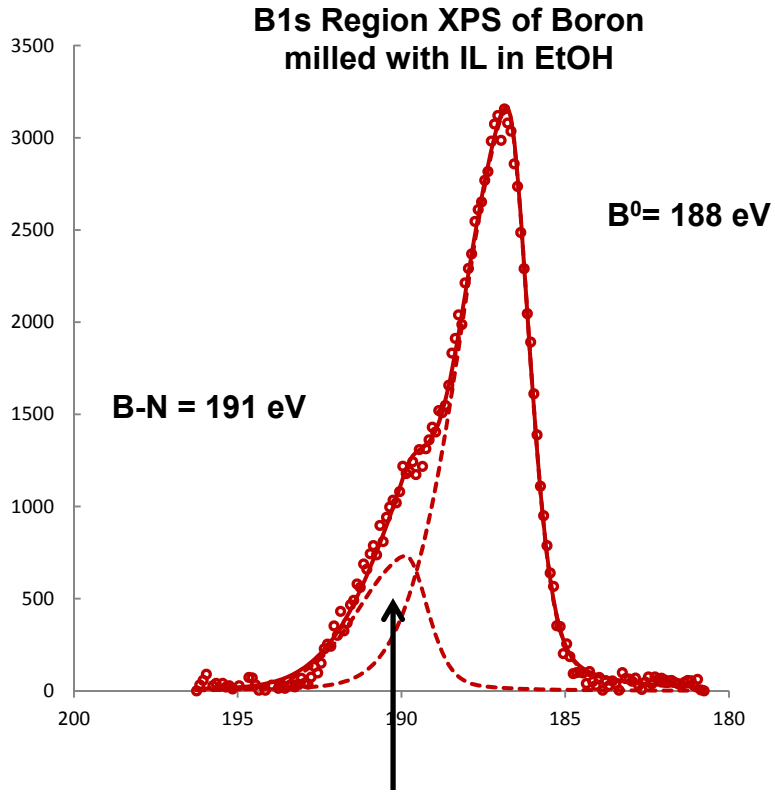
B1s Region XPS of Boron milled in EtOH w/o any surfactant

Boron powder milled in EtOH w/o surfactant

Indicates surface oxidation of BNP

IL/metal hybrid fuels

BNPs form stable suspensions in 1-methyl-4-amino-1,2,4-triazolium dicyanamide (MAT-dca)



Indicates chemisorption of IL to BNP?

Boron powder milled in EtOH w/ MAT DCA

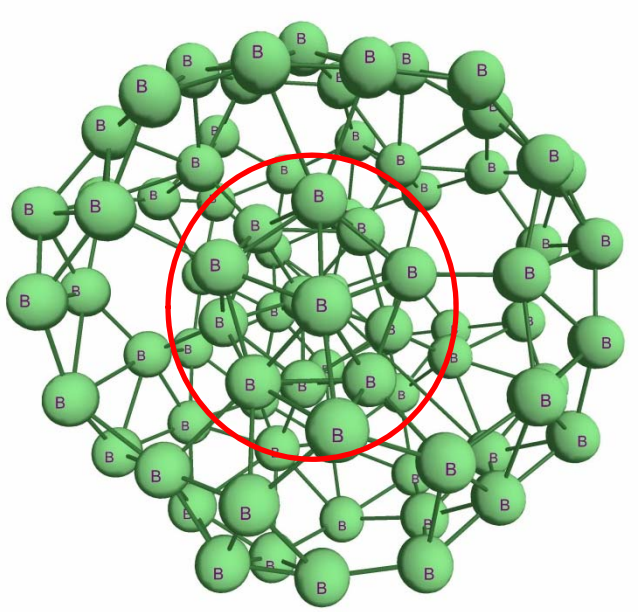
IL/metal hybrid fuels

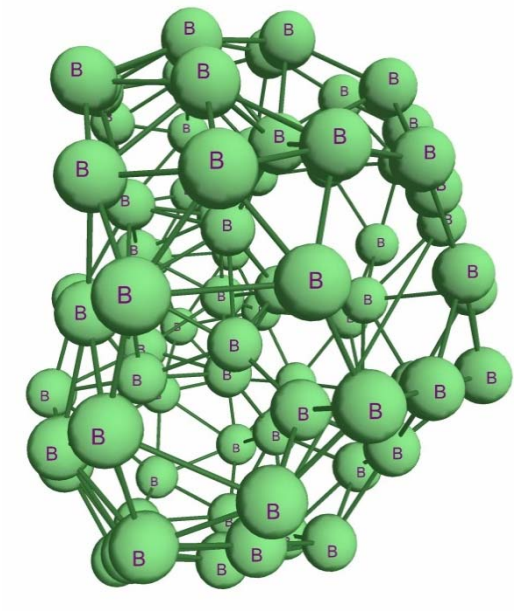
- **Why do BNPs form stable suspensions in some solvents/ILs but not others?**
- **What types of chemical interactions occur between solvent/IL and BNPs?**
- **Can we predict which solvents/ILs will inhibit oxide layer formation in BNPs?**

IL/metal hybrid fuels

Computational model

- B_{80} cluster used to represent BNP
- Single solvent molecule or IL ion pair
- Calculate structure and interaction energies
  - Correlation between interaction energy and formation of stable colloid?





IL/metal hybrid fuels

Computational model – why B_{80}??

- Calculations predict most stable forms of B_n for n < 20 are quasi-planar
- Most stable form of B_{20} is a ring

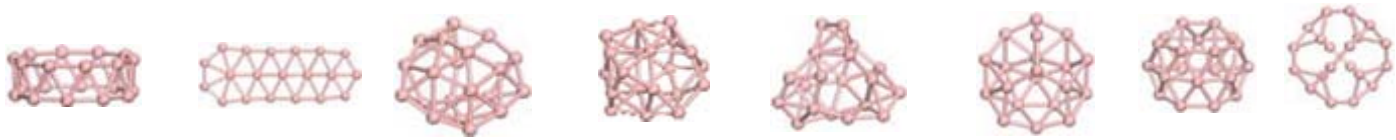


Table I. The MP2/6-311G* optimized B_{20} geometries and computed relative energies (in eV) of the eight B_{20} isomers at different theoretical levels.t1n1

Symmetry	C_{5v}	C_{2v}	C_2	C_1	C_1	C_s	C_s	S_4
CCSD(T)	0	0.72	1.46	1.87	1.97	2.31	2.80	3.45
MP2	0	1.13	1.07	0.94	1.89	1.47	1.16	3.32
PBE	0	0.67	1.51	1.69	2.26	2.52	2.60	3.80
TPSS	0	0.68	1.66	1.96	2.17	2.46	3.00	3.35
TPSSh	0	0.79	1.65	1.93	2.12	2.44	3.09	3.23
PBE0	0	0.96	1.50	1.68	2.13	2.47	2.90	3.53
mPW1PW91	0	0.99	1.75	2.15	2.37	2.74	3.74	3.75
M06-2X	0	1.11	1.03	0.93	1.61	1.98	1.13	2.71
B3LYP	0	0.99	3.25	4.24	3.82	4.39	4.80	5.34
BLYP	0	0.75	3.38	4.39	4.04	4.58	4.78	5.63

Fengyu Li, Peng Jin, De-en Jiang, Lu Wang, Shengbai B. Zhang, Jijun Zhao, and Zhongfang Chen, J. Chem. Phys. 136, 074302 (2012)

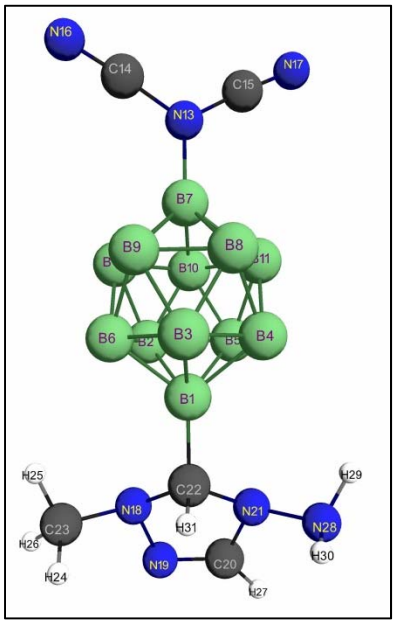
IL/metal hybrid fuels

Computational model – why B_{80}??

- IL interactions with small 3D clusters (e.g., B_{12}) inconsistent with larger clusters

B_{12} + [MAT][DCA]

E_{int} = 104.5 kcal/mol

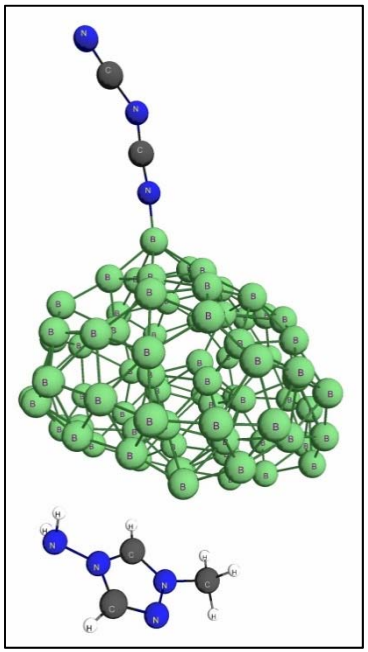


Distinct differences in

- interaction energies (2x)
- binding of cation
- binding of anion

B_{80} + [MAT][DCA]

E_{int} = 51.5 kcal/mol

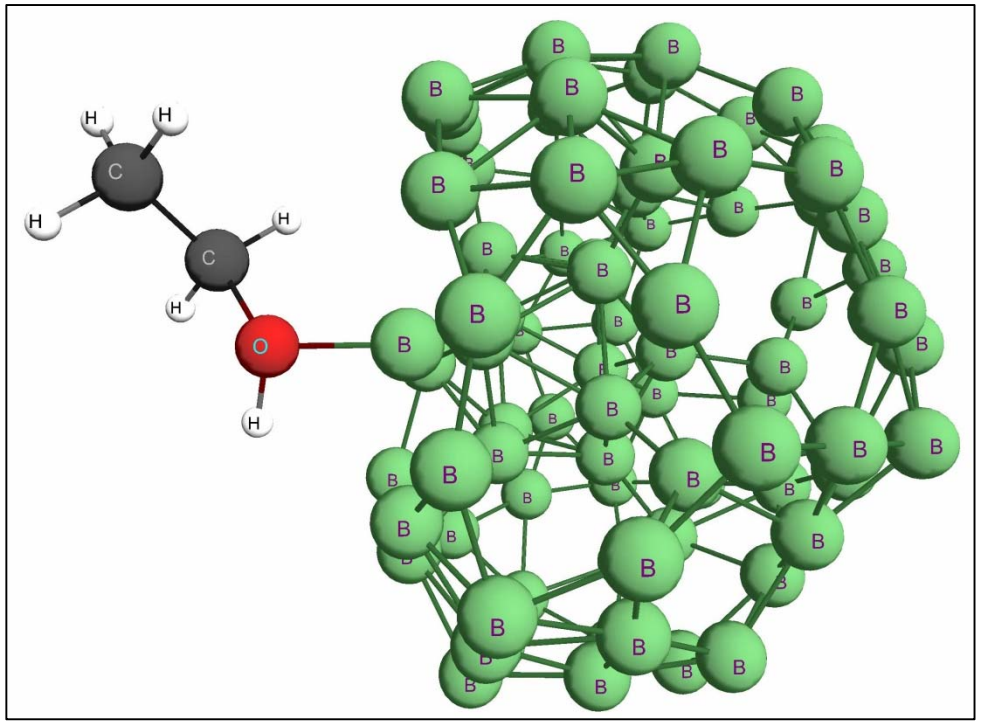


IL/metal hybrid fuels

How do nonionic solvents interact with BNPs?

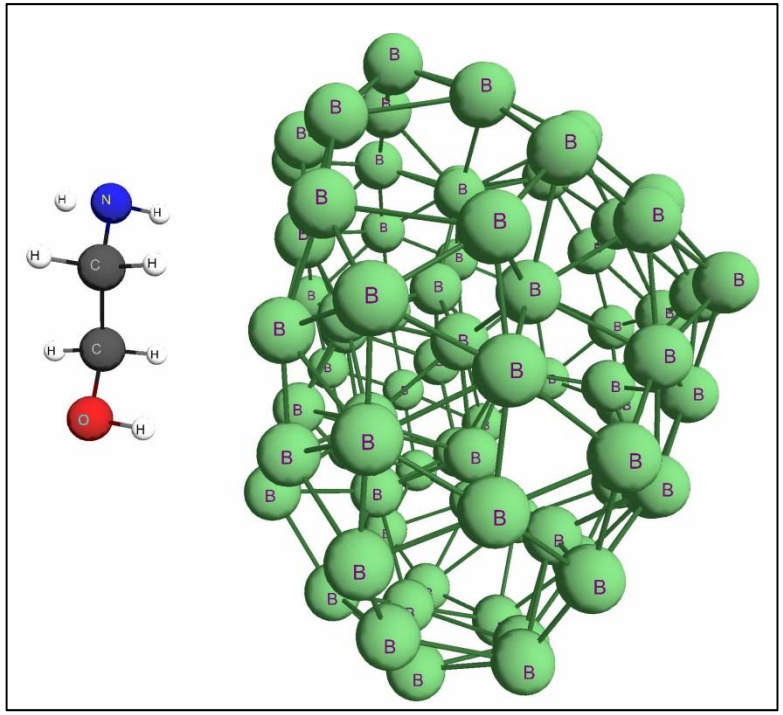
B_{80} + ethanol

E_{int} = 14.9 kcal/mol



B_{80} + ethanolamine

E_{int} = 4.2 kcal/mol

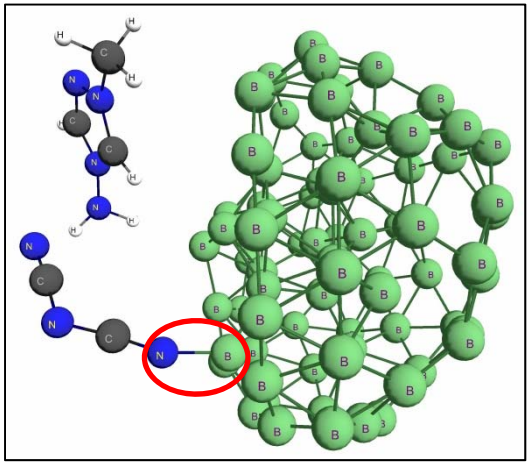


IL/metal hybrid fuels

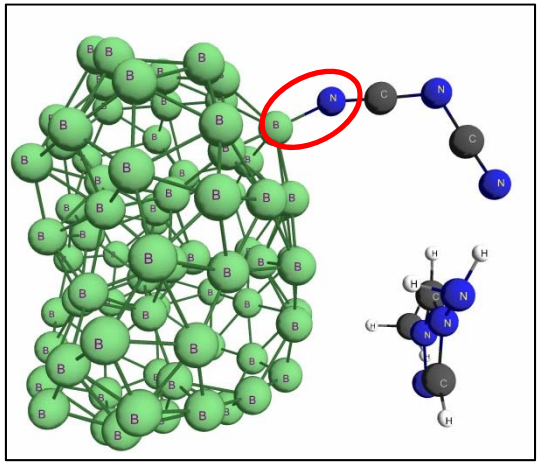
How do ionic solvents interact with BNPs?

B_{80} + MAT-dca

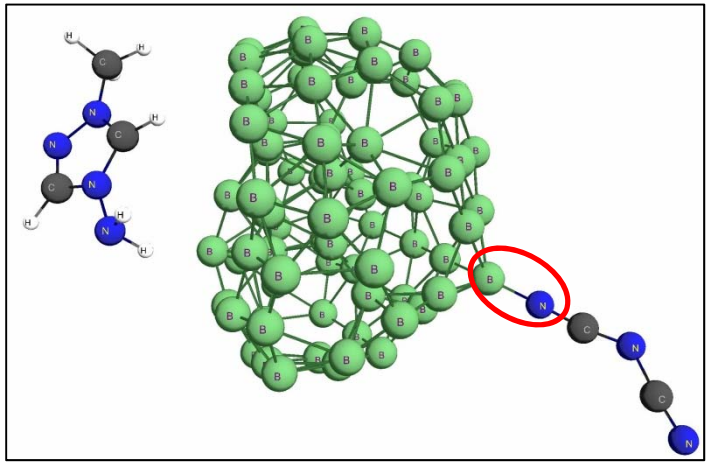
E_{int} = 39.2 kcal/mol



E_{int} = 30.1 kcal/mol



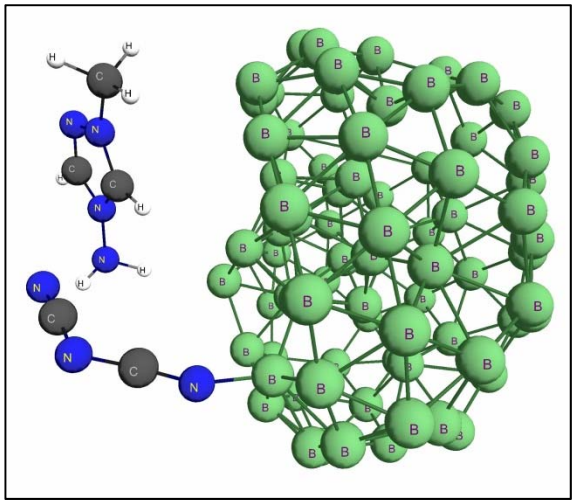
E_{int} = 50.3 kcal/mol

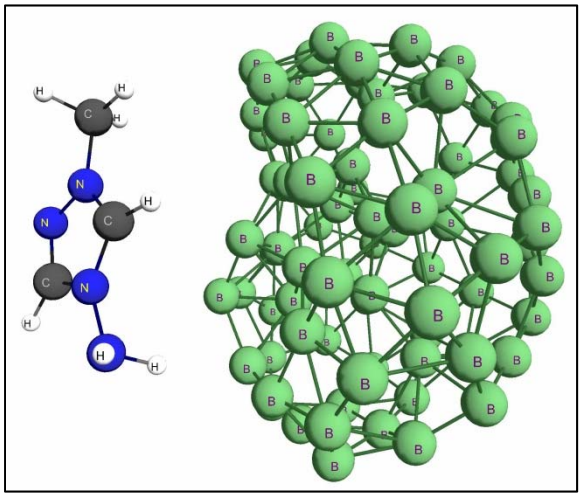


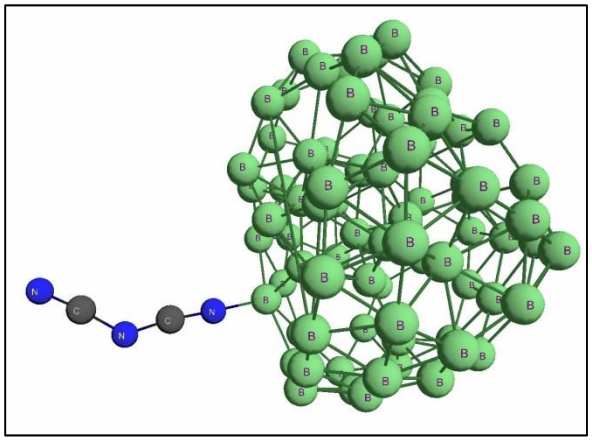
EIL interactions with B_{80}

Role of IL cation vs anion

Cation + anion	Cation only	Anion only
E_{int} = -45.5 kcal/mol	E_{int} = -27.5 kcal/mol	E_{int} = -58.7 kcal/mol



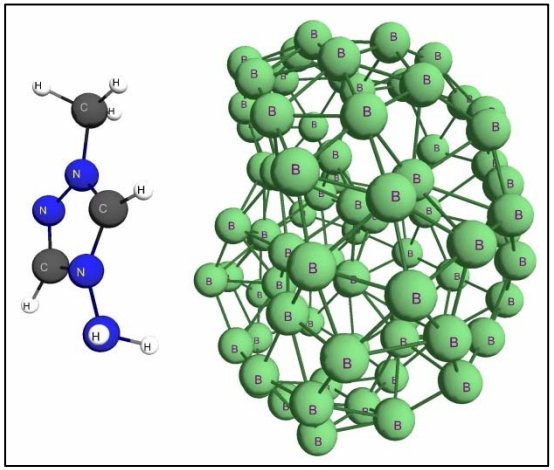
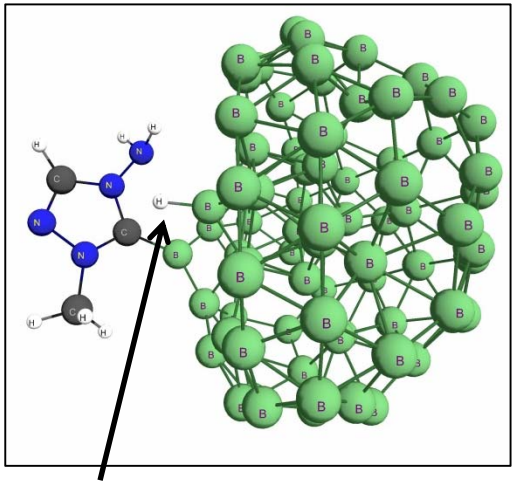
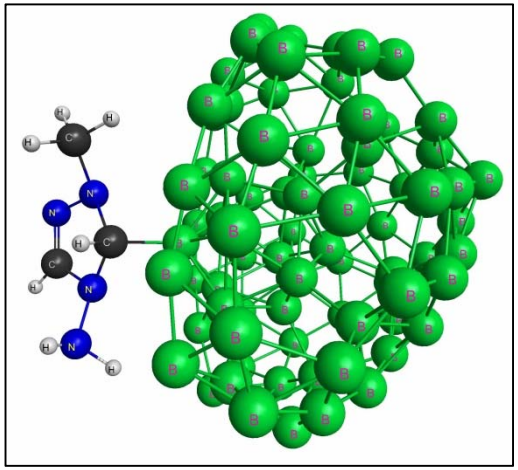




Electron-rich anion interacts more strongly with BNPs (e- deficient)

EIL interactions with B_{80}

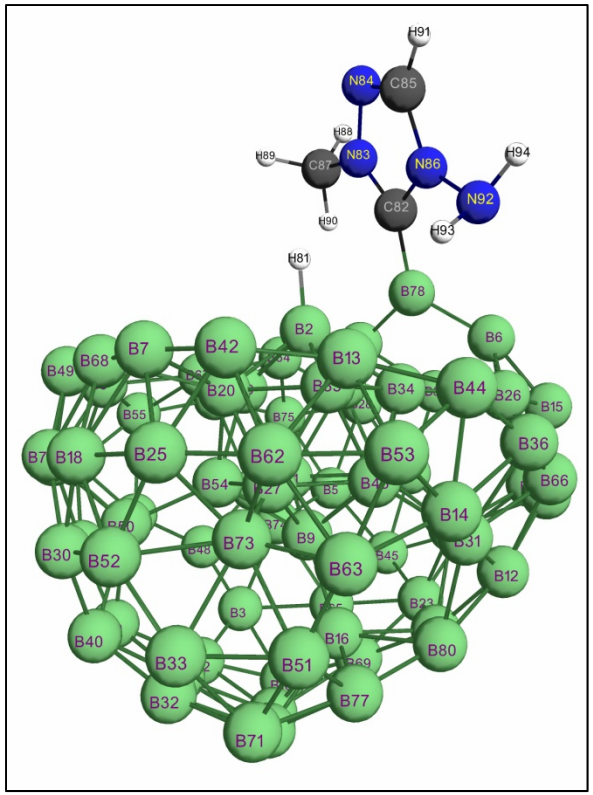
IL cation:BNP interactions – a deeper look

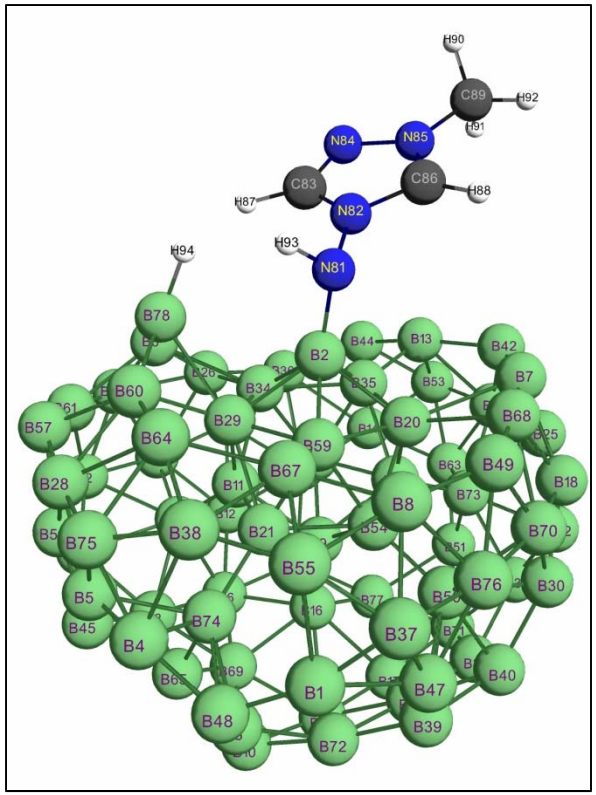
E_{int} = -27.5 kcal/mol	E_{int} = -61.8 kcal/mol	E_{int} = -35.2 kcal/mol
		
Covalent bond to B_{80} surface not present	H-atom transfer from cation to B_{80}, C-B bond formed	C-B bond to B_{80} surface is formed

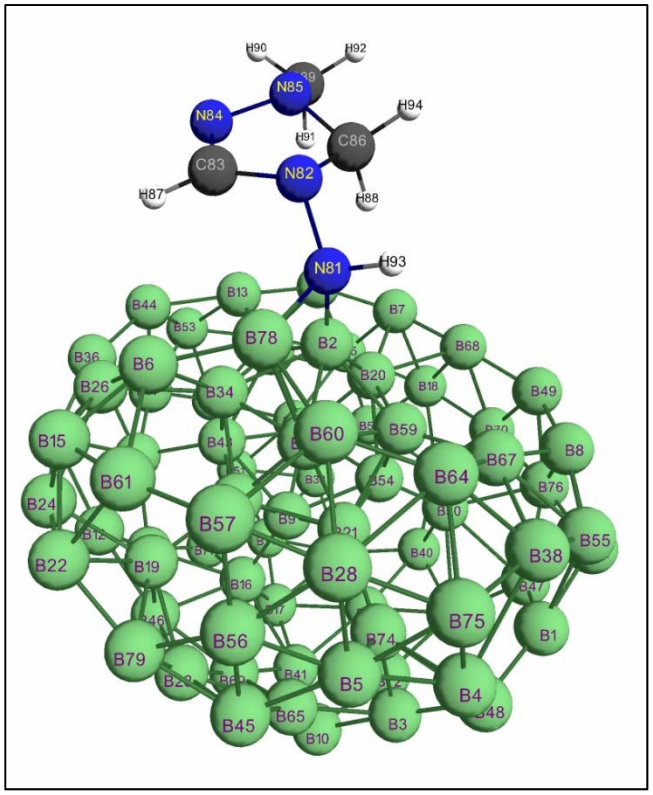
Cation can form covalent bond to BNP, but likely has to overcome energy barrier (calculation of barrier in progress)

IL/metal hybrid fuels

- **Is proton transfer from MAT$^+$ to the BNP possible? (YES)**
  - If so, what are the reaction barriers? (TBD)

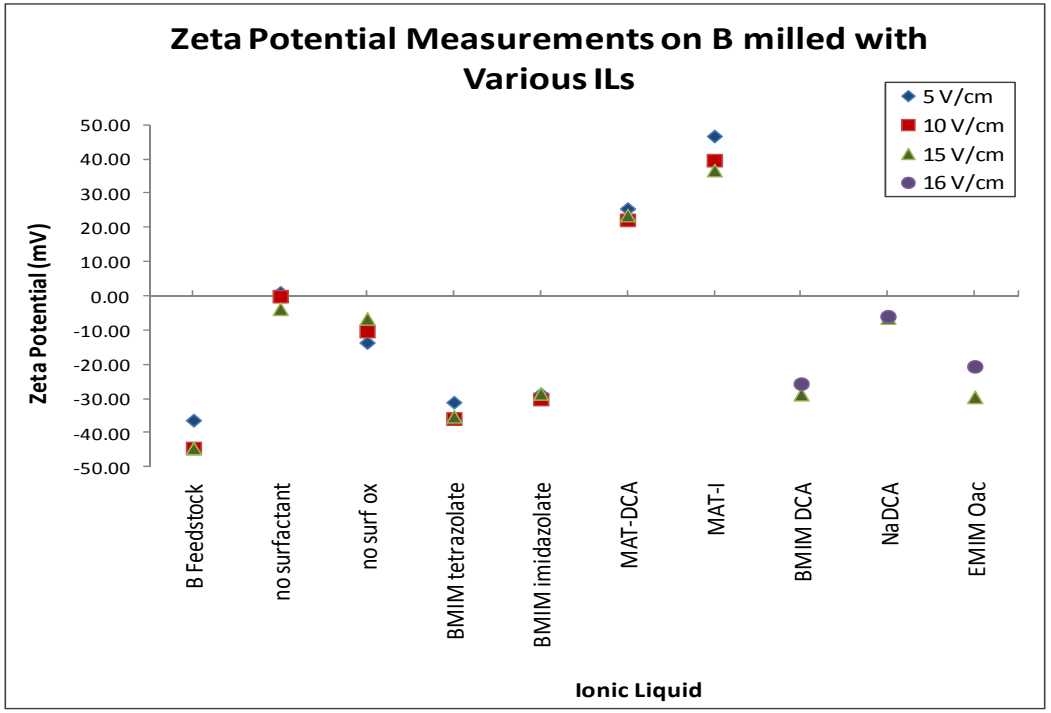


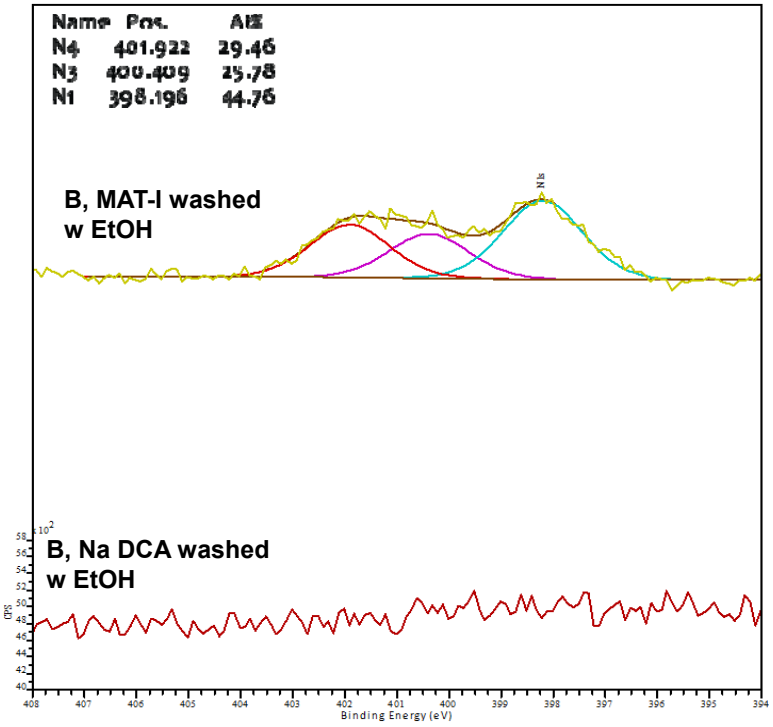




IL/metal hybrid fuels

- **Calculations predict strong interactions between DCA^- and BNP.**
  - MAT^+ essentially a “spectator”
  - Contrary to some experimental results (zeta potentials, XPS spectra)





IL/BNP hybrid fuels: Summary

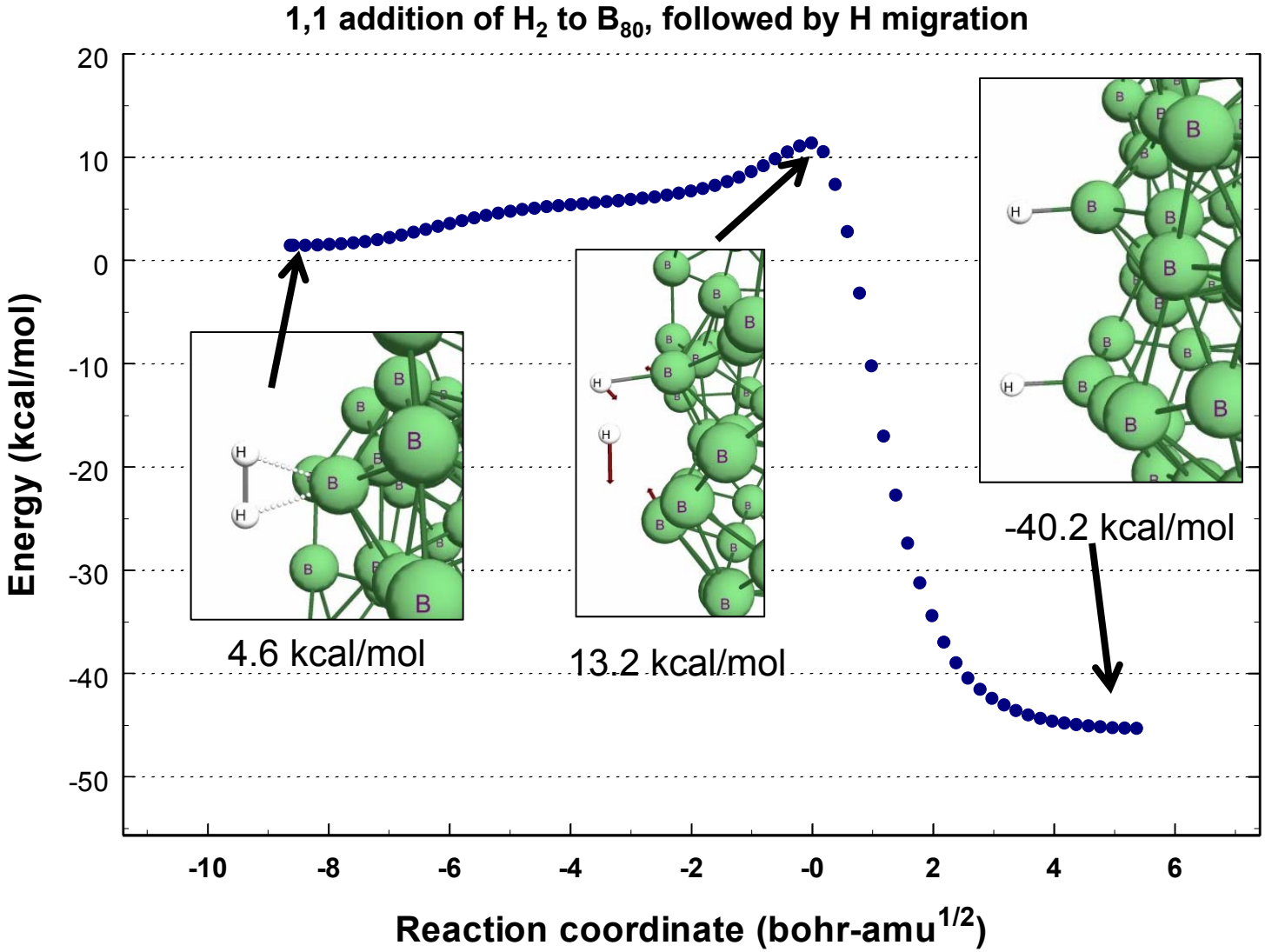
- **ILs interact more strongly with BNPs than nonionic solvents such as ethanol, ethanolamine**
  - Consistent with observed passivation of BNP milled with MAT-DCA and formation of stable colloidal suspensions of BNPs in ILs.
- **Proton transfer from MAT^+ to BNP is thermodynamically favorable**
  - Comparable to interaction energies of DCA^- with BNP.
  - Reaction barriers still to be determined.
- **Multiple types of interactions between ILs and BNPs are possible**
  - Covalent bond formation between DCA- and BNP occurs with little or no barrier
  - Formation of covalent bond between MAT^+ and BNP is favorable, but likely encounters a barrier (TBD).

Improved dispersion of NPs in ILs

- **Ball milling of BNPs in presence of H_2 leads to formation of B-H surface passivated layer**
  - Calculations predict barrier of 10 kcal/mol, and exothermicity of 35 kcal/mol for chemisorbed H_2 to dissociate to form two H-B_{surf} .
- **Observed H_2 uptake in boron ball milling of 5 wt % (36 mol %) consistent with formation of saturated H-terminated BNP surface**
  - Calculations show that formation of $H_{58}B_{80}$ is exothermic by 710 kcal/mol.
- **B-H functionalized BNPs react with alkenes and N-rich ILs**
  - facilitates dispersion of capped BNPs in polar and non-polar liquids

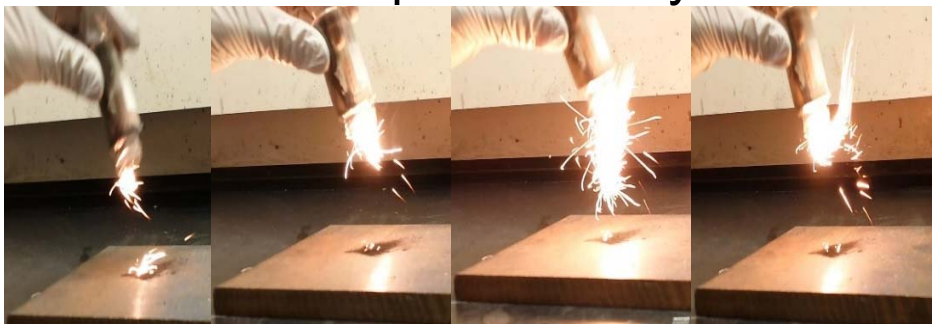
Perez et al., ACS Appl. Mater. Interfaces, 2015, 7, 9991-10003.

Formation of H-terminated BNPs



Next step: Al nanoparticles

- Aluminum nanoparticles (NPs) are of interest as energetic ingredients in explosives and propellant formulations, due to high energy density, enhanced burn rates due to high surface/volume ratio, etc.
- Efficient, gram-level production of Al nanoparticles via ball milling is obtained using NH_3, CH_3NH_2, CH_3CN, B_2H_6, etc., as milling agents.
- Milling agents decompose on Al NP surface to produce gaseous products and surface-bound species.
- Milling/capping agents can also inhibit formation of inert oxide layer on NP surface.
- Surface-coated NPs can be functionalized to enhance/control NP dispersion in hydrocarbons, ILs, etc.



Spontaneous combustion of Al nanoparticles milled in CH_3CN, upon exposure to air.

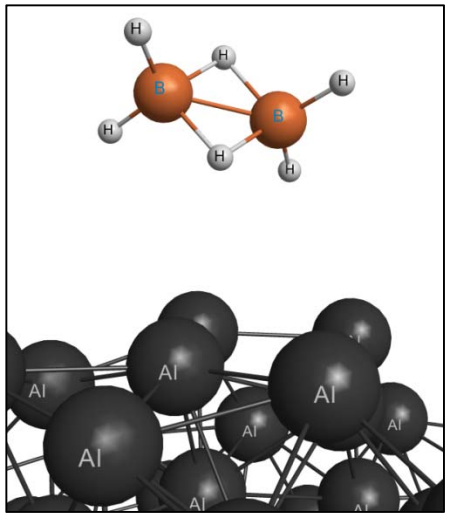
Ball milling gaseous byproducts

Aluminum nanoparticle production, in presence of milling agent

Milling agent → Gaseous byproducts ↓	NH_3	CH_3NH_2	CH_3CN	B_2H_6
H_2	√	√	√	√
CH_3NHCH_3		√		
CH_2NH		√		
CH_4			√	
CH_3CH_3			√	

Can theory explain, for example in the case of B_2H_6 as the milling agent, the predominant formation of H_2 as the only observed gaseous byproduct?

B_2H_6 physisorbed/chemisorbed on Al_{80}



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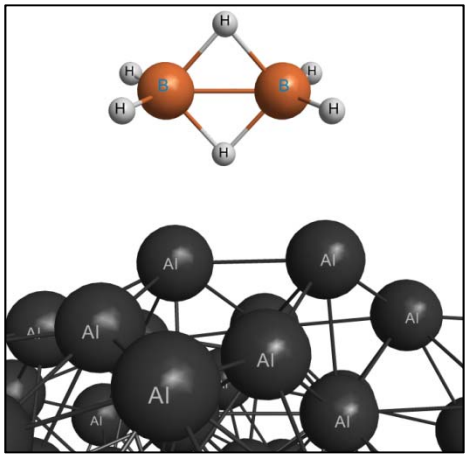
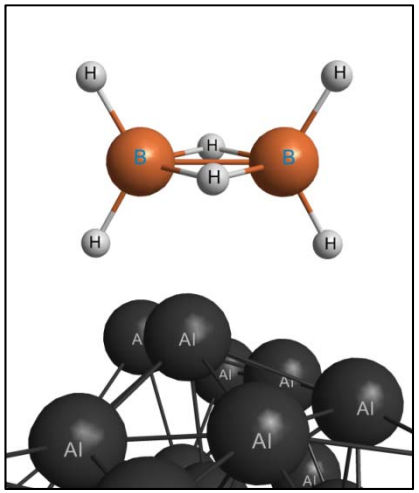


-4.1 (-3.8)



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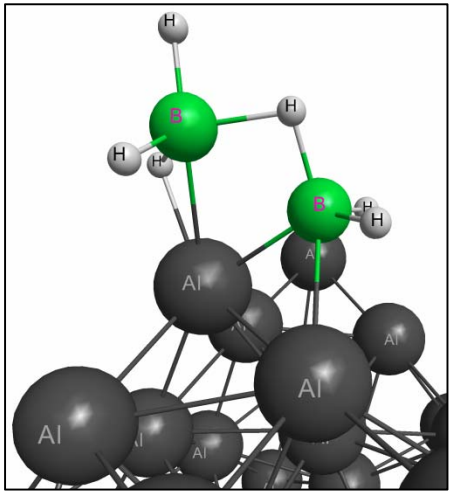

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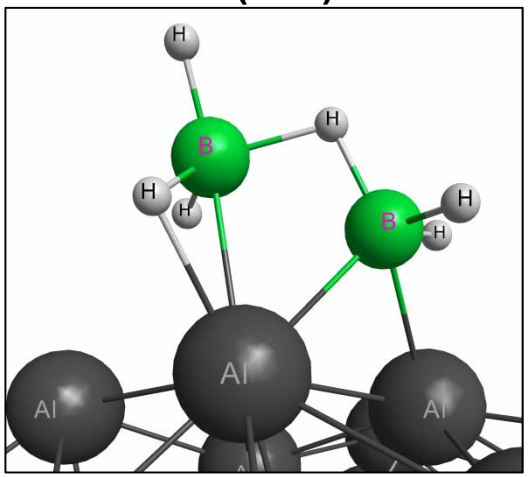

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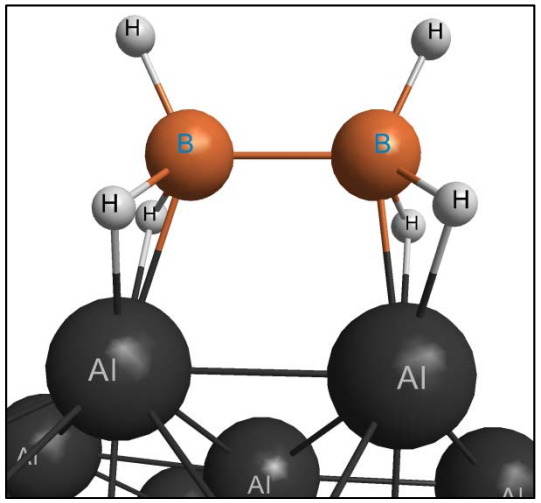
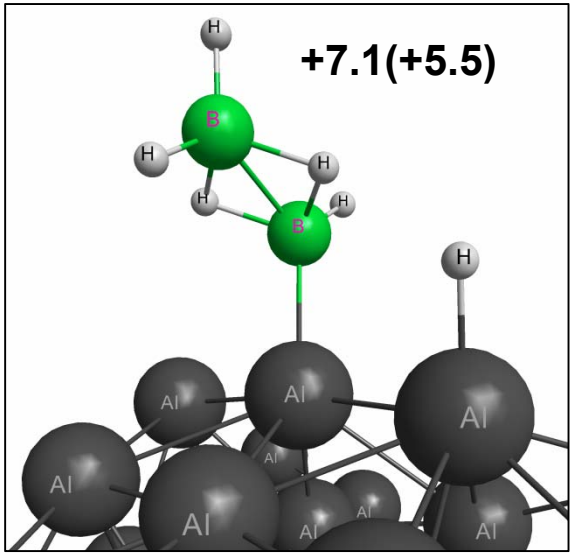
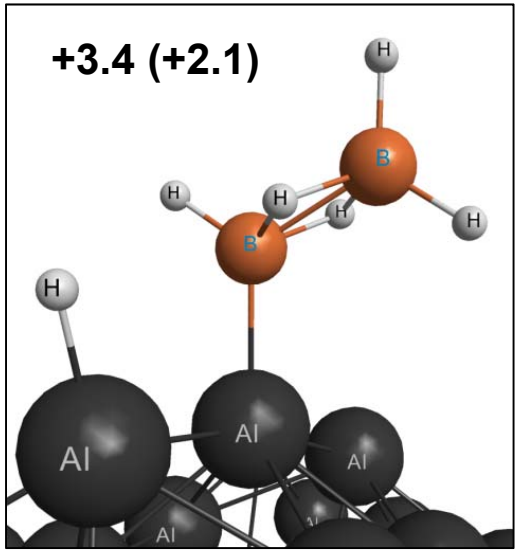
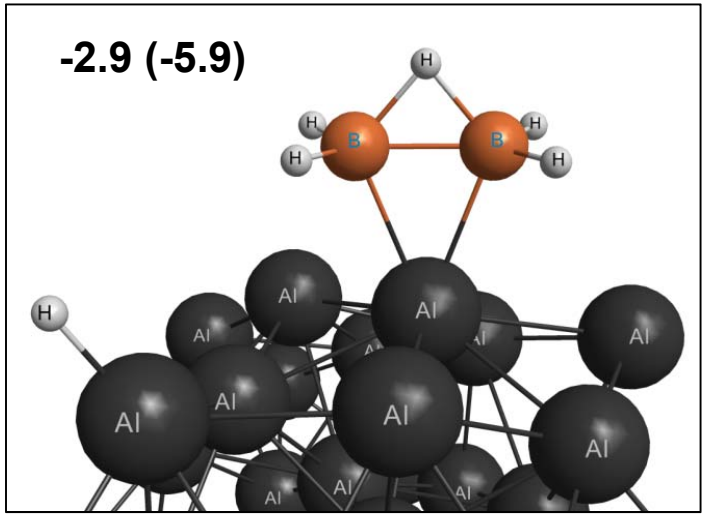


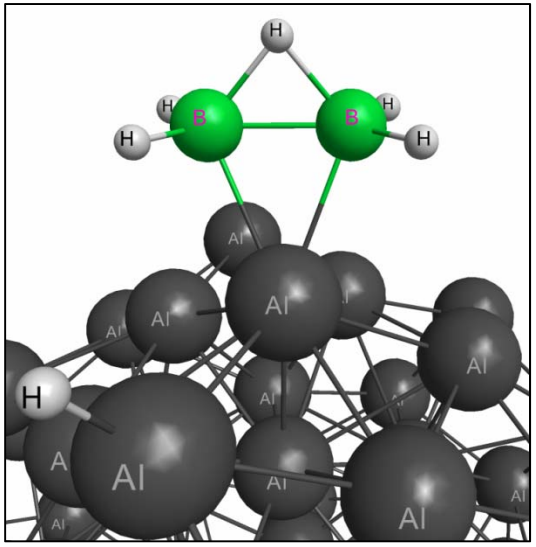
-7.4 (-8.4)

B_2H_5 + H chemisorbed on Al_{80}

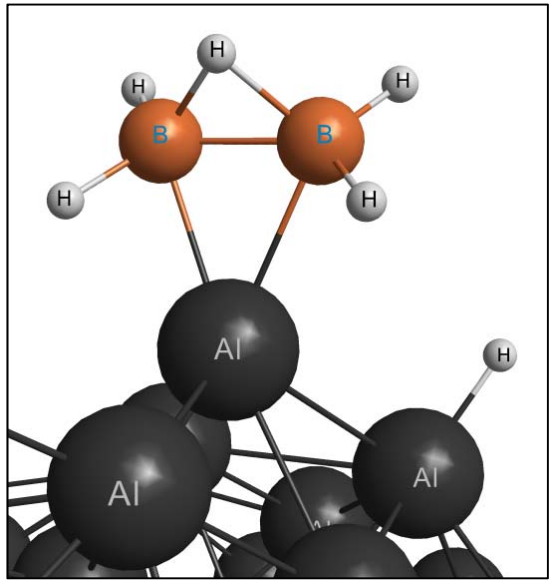






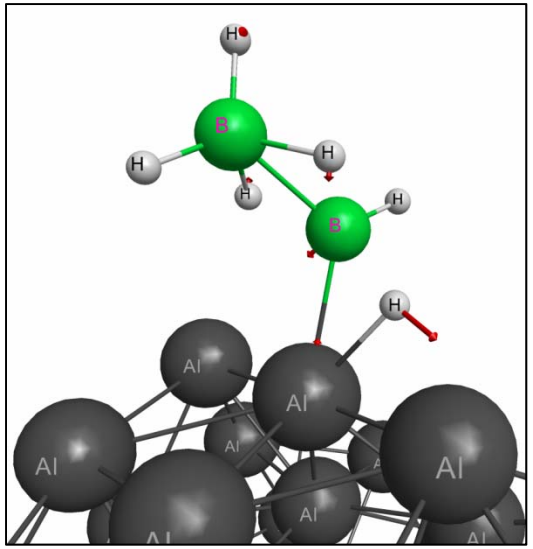


-6.7 (-9.5)

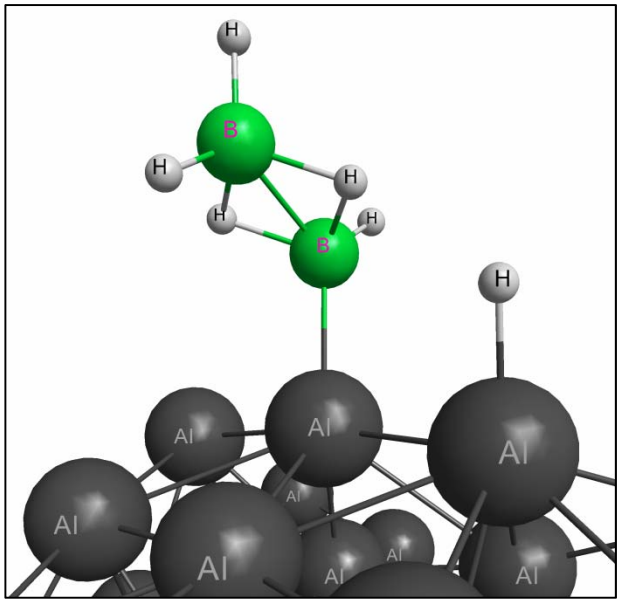


-7.7(-10.4)

$B_2H_6{:}Al_{80} \rightarrow B_2H_5\text{-}Al_{80}\text{-}H$



29.5(26.2)

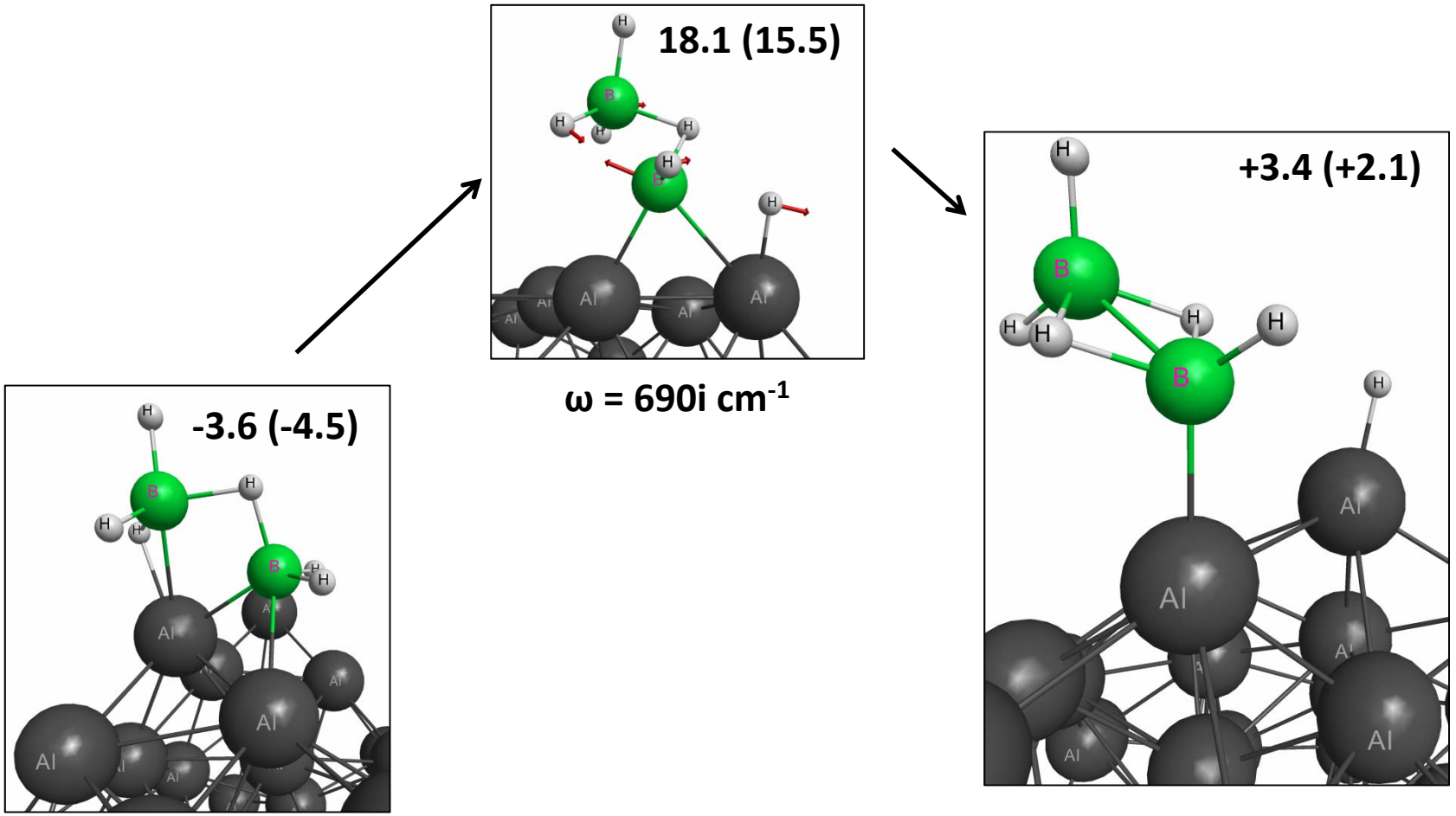


7.1(5.5)

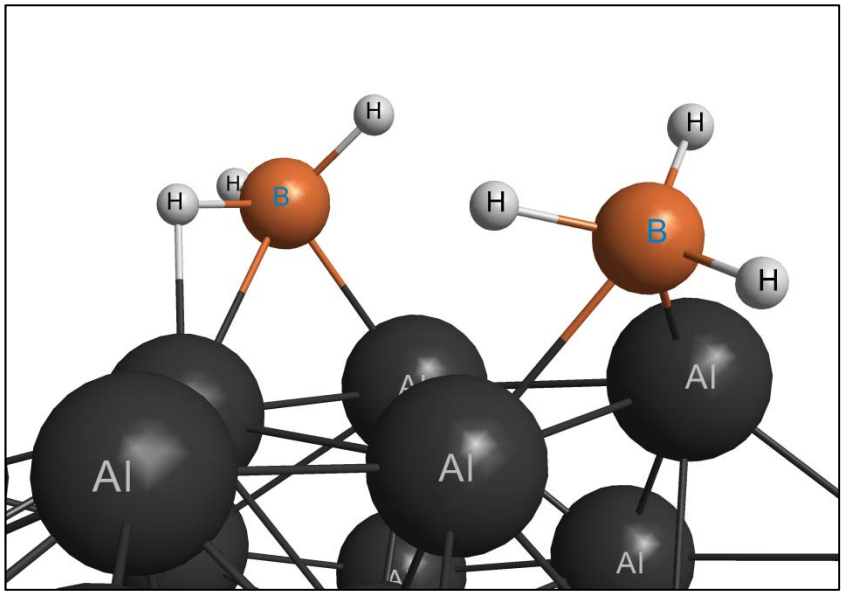
$Al_{80} + B_2H_6$

0.0 (0.0)

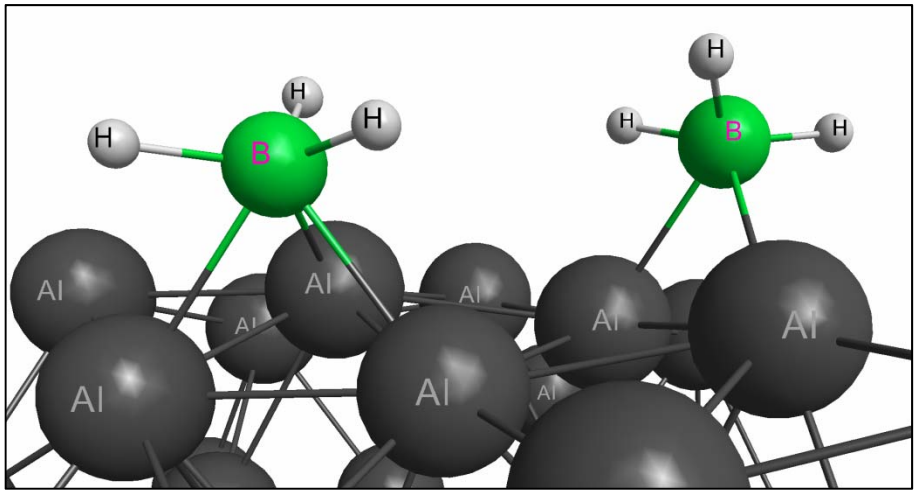
$B_2H_6{:}Al_{80} \rightarrow B_2H_5\text{-}Al_{80}\text{-}H$



BH_3-Al_{80}-BH_3

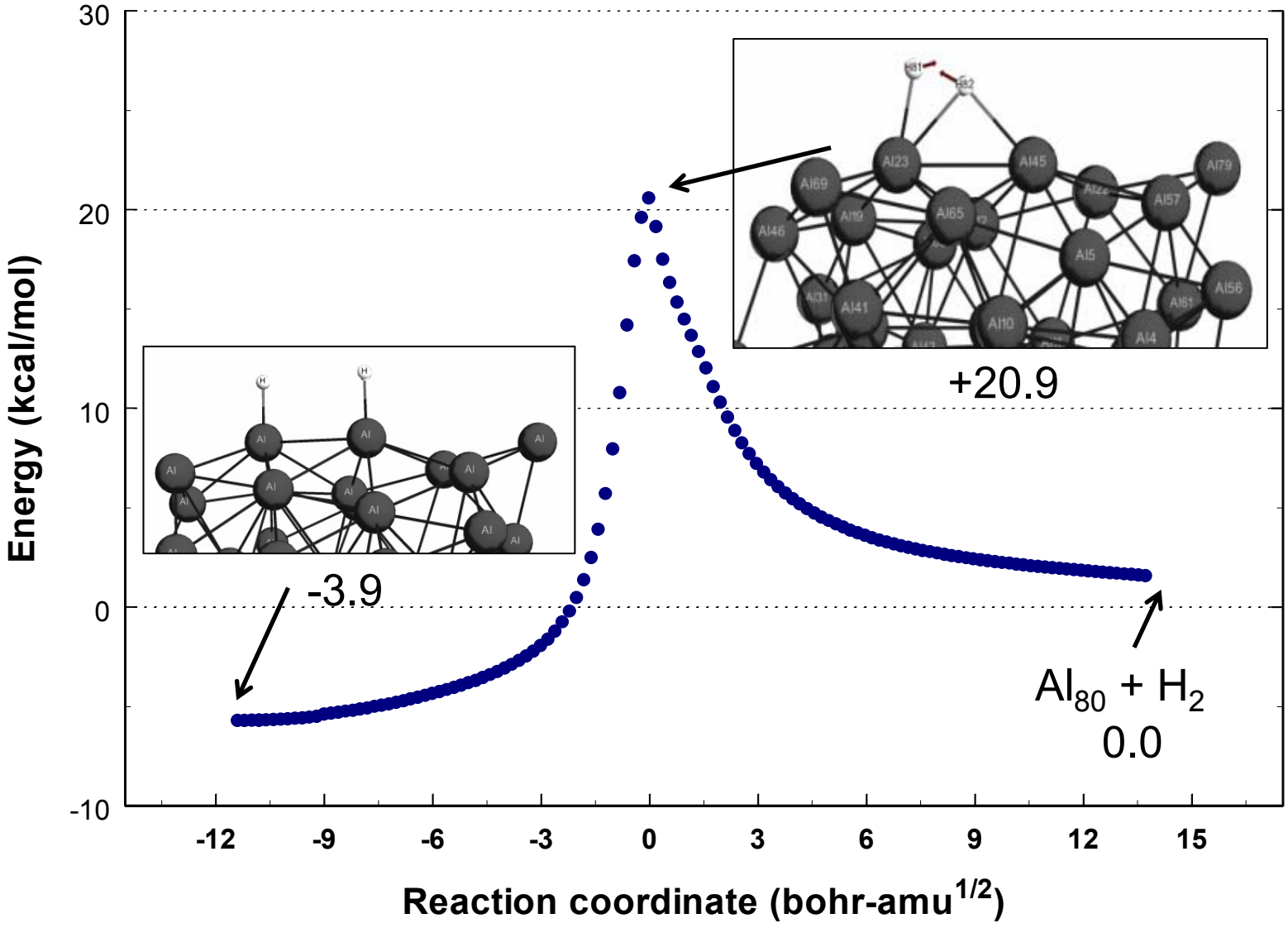


-7.5 (-10.8)



-2.1 (-5.2)

$2H:Al_{80} \rightarrow Al_{80} + H_2$



Summary and Conclusions

- **Production of Al nanoparticles via ball milling with B_2H_6**
  - B_2H_6-assisted ball milling of Al powder efficiently produces Al NPs, with H_2 as the predominant byproduct.
  - Surface reactions of B_2H_6 on Al_{80} have been modeled using DFT
    - B_2H_6 physisorbs and chemisorbs to Al_{80} with binding energies of 3-8 kcal/mol
    - Fragmentation of bridging B-H bonds is exothermic (6-11 kcal/mol)
    - Fragmentation of terminal B-H bonds is endothermic (2-6 kcal/mol)
    - B-H fragmentation barriers are 20-26 kcal/mol
    - B-B fragmentation to form chemisorbed BH_3 is exothermic (5-11 kcal/mol)
    - Formation of H_2 via recombination of chemisorbed H atoms is endothermic by 4 kcal/mol and crosses a barrier of 25 kcal/mol
    - B-H fragmentation and subsequent H-H recombination have similar barriers, both of which are energetically accessible under experimental ball milling conditions

Acknowledgements

- **Collaborators**
  - Univ. of Utah: Scott Anderson, ...
  - McGill Univ.: Robin Rogers, ...
  - AFRL: Stefan Schneider, Gammy, Steve Chambreau....

- **GRC organizers**
  - Prof. Mudring

- **Support**
  - AFOSR
  - DoD HPC Modernization Program

Backup Slides

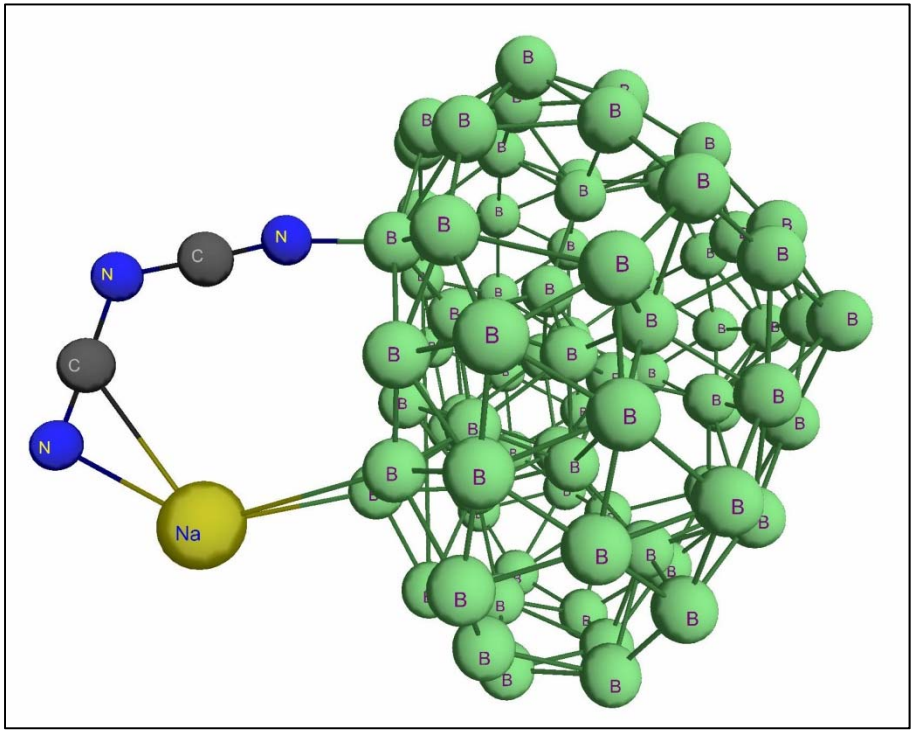
IL/metal hybrid fuels: summary

Solvent/IL + BNP	Forms stable emulsion?	Passivates NP surface?	Calculated interaction energy (kcal/mol)
EtOH	No	No	14.9
$NH_2CH_2CH_2OH$	??	??	4.2
BMIM-DCA	Yes	No	n/a
Na-DCA	??	No	47.8
MAT-DCA/EtOH	Yes	Yes	30.1, 39.2 (MAT DCA only; no EtOH)
MAT-I/ACN	??	No	54.0 (no ACN)
MAT-NTf2	TBD	TBD	TBD
MAT-NCA	TBD	TBD	TBD
MAT-acetate	TBD	TBD	TBD

IL/metal hybrid fuels

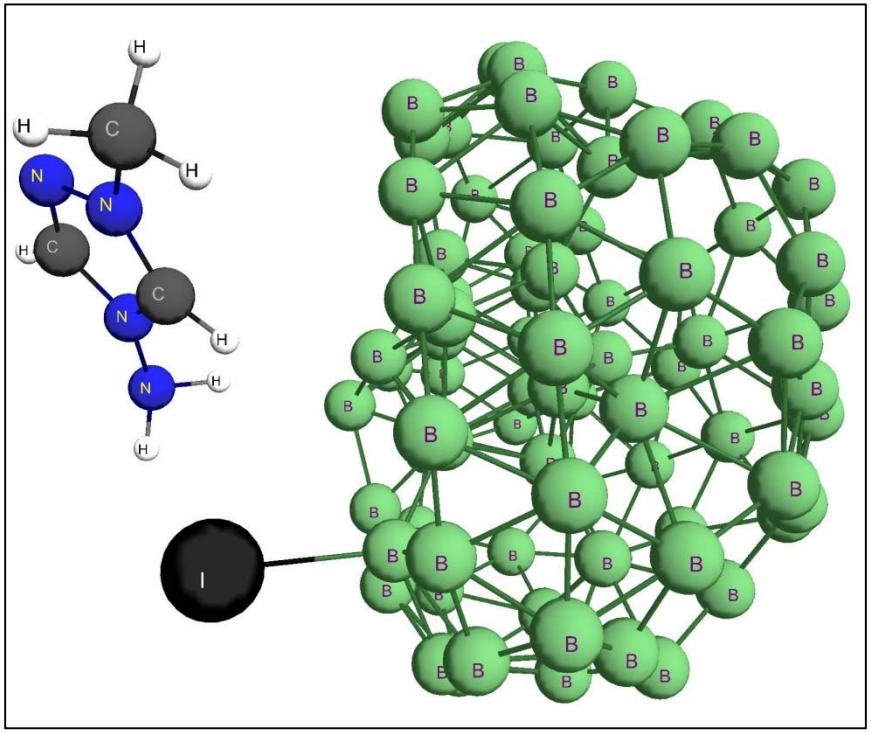
B_{80} + Na-dca

E_{int} = 46.6 kcal/mol



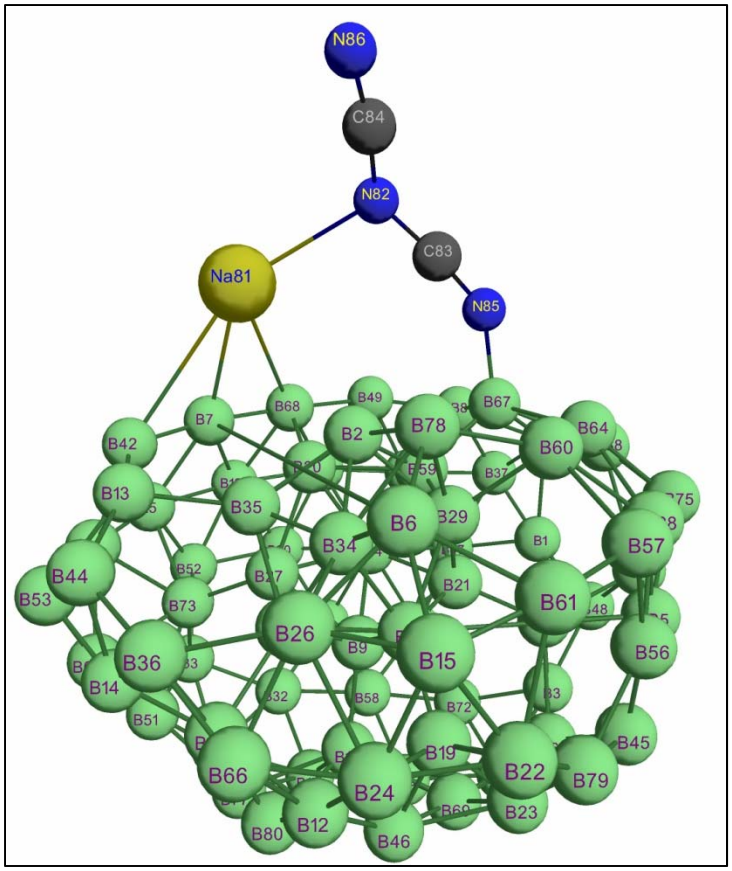
B_{80} + MAT-I

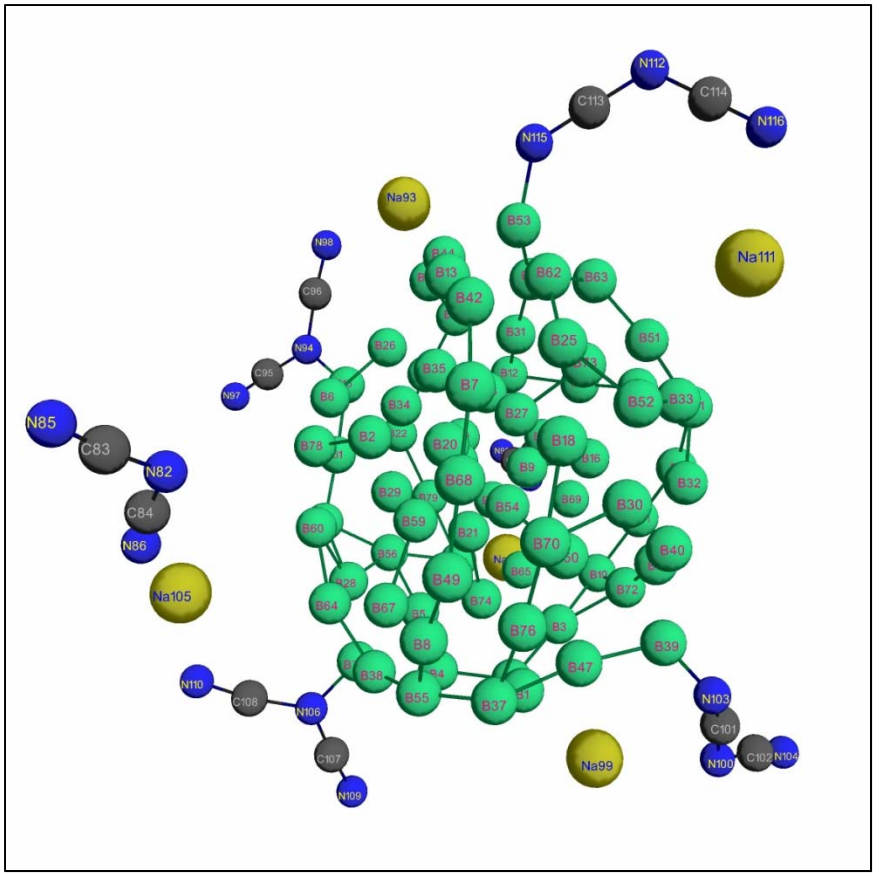
E_{int} = 23.0 kcal/mol



IL/metal hybrid fuels

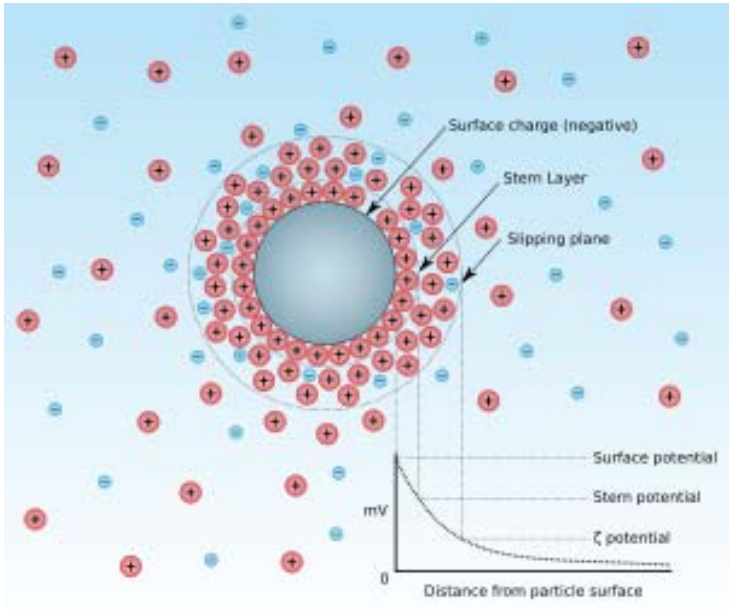
Do multiple ion pairs change the nature of the IL/BNP interactions? (YES)





Zeta Potentials

Zeta potential is a scientific term for electrokinetic potential[1] in colloidal systems. In the colloidal chemistry literature, it is usually denoted using the Greek letter zeta, hence ζ-potential. From a theoretical viewpoint, zeta potential is electric potential in the interfacial double layer (DL) at the location of the slipping plane versus a point in the bulk fluid away from the interface. In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle.



A value of 25 mV (positive or negative) can be taken as the arbitrary value that separates low-charged surfaces from highly-charged surfaces.

The significance of zeta potential is that its value can be related to the stability of colloidal dispersions (e.g., a multivitamin syrup). The zeta potential indicates the degree of repulsion between adjacent, similarly charged particles (the vitamins) in a dispersion. For molecules and particles that are small enough, a high zeta potential will confer stability, i.e., the solution or dispersion will resist aggregation. When the potential is low, attraction exceeds repulsion and the dispersion will break and flocculate. So, colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate as outlined in the table.